

Modelling spin qubits in carbon peapods

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We have calculated electron spin interactions in chains of Sc@C₈₂ endohedral fullerenes in isolation and inserted into a semiconducting or metallic single-walled carbon nanotube to form a peapod. Using hybrid density functional theory (DFT), we find that the spin resides mainly on the fullerene cage, whether or not the fullerenes are in a nanotube. The spin interactions decay exponentially with fullerene separation, and the system can be described by a simple antiferromagnetic Heisenberg spin chain. A generalised Hubbard-Anderson model gives an exchange parameter J and a Coulomb parameter U in good agreement with the DFT values. Within the accuracy of the calculations, neither semiconducting nor metallic nanotubes affect the interactions between the fullerene electron spins.

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Spin qubits have potential for controlled interactions [1] for quantum computing. Carbon is a candidate host for spin qubits because in ¹²C materials the small spin-orbit coupling and absence of hyperfine coupling ensures long spin coherence times. Carbon peapods [2], that is, single-walled carbon nanotubes (SWNT) containing fullerenes, have been proposed as hosts for spin-qubits [3]. The fabrication of nanoscale electronic devices such as field effect transistors with carbon peapods containing various endohedral fullerenes is well established [4]. When spin active metallic atoms such as Sc are incarcerated in a carbon cage, the system develops hybridized orbitals resulting in an unpaired electron delocalized across the fullerene cage [5]. Here we report on detailed numerical simulations which establish the nature of the spin-spin interactions both between endohedral fullerenes and between fullerenes and nanotubes. The dominant interaction is of the Heisenberg form, which is known to be suitable for quantum computing (QC) in one-dimensional chains [6]. Moreover, these results support this system to be promising for experimentally-proven QC protocols which allow chains formed of identical units to be controlled “globally” [7], i.e. without the need to target individual units, leading to a scalable molecular quantum computer.

Four fundamental problems need to be understood in order to demonstrate well-defined qubits in carbon peapods as proposed in Ref. [8]: (i) the charge arrangement within the carbon peapods; (ii) the electron spin distribution; (iii) the coupling between spin-qubits; (iv) the nature of the spin interactions between fullerenes and nanotube. Density functional theory (DFT) calculations have been reported on several model systems, such as SWNT containing C₆₀, K_xC₆₀, Y@C₆₀, C₈₂ and La@C₈₂ [9, 10, 11, 12, 13, 14]. To date little work

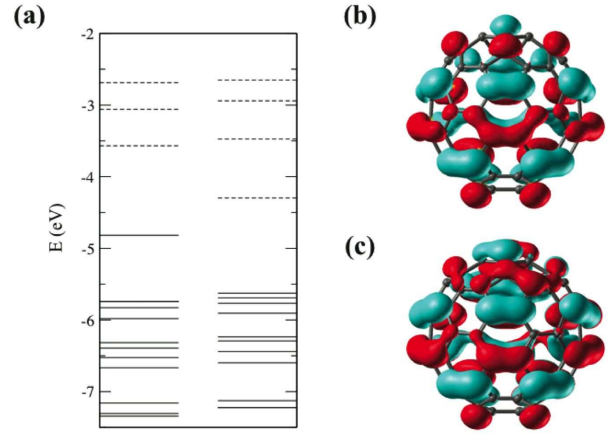


FIG. 1: (Color online) (a) Eigenspectrum of relaxed Sc@C₈₂ molecule. Left (right) hand side refers to spin-up (-down) electrons. Solid (dashed) lines refer to occupied (unoccupied) energy levels. (b) HOMO of relaxed Sc@C₈₂. (c) LUMO+1 of relaxed C₈₂. Dark grey (red online) and light grey (blue online) lobes represent positive and negative phases.

has been done on understanding the spin properties of peapods and the above mentioned issues (ii), (iii) and (iv) have not been addressed in detail thus far. We have computed the charge and spin distributions and the electronic structures within Sc@C₈₂ chains and peapod structures. We find well-defined spin-1/2 qubits on the fullerenes, with strong evidence for a nearest-neighbor Heisenberg exchange interaction. We can tune this exchange interaction strength by controlling the inter-fullerene spacing during synthesis. In order to describe the influence on the spin-qubits localized on the fullerenes from propagating electrons or holes in the nanotube, we need to go beyond

DFT to a model which is capable of describing the low-energy charge-spin excitations of the system. We conjecture a generic Hubbard-Anderson model, which has these properties, to estimate the low-energy spin interactions; in particular the Heisenberg exchange between spins along the fullerene chain and the Kondo exchange interaction between localized spins on the fullerenes and spins of propagating electrons or holes in the nanotube.

As model systems, we choose Sc@C_{82} in (14,7) (semiconducting) and (11,11) (metallic) SWNTs. Our calculations predict an exothermic encapsulation of Sc@C_{82} for both tubes. The repeat units containing one Sc@C_{82} molecule in the (14,7) and (11,11) peapods are 11.42 Å and 12.47 Å, respectively [15]. In order to study the exchange interaction, we use double unit cells containing two Sc@C_{82} molecules. The interwall separations between the (14,7) and (11,11) tubes and Sc@C_{82} are 3.35 Å (van der Waals distance) and 3.55 Å, respectively. The relaxed structure of Sc@C_{82} is found to be in agreement with Ref. [5] with a Sc-C distance of 2.26 Å. The DFT calculations are performed with the hybrid exchange density functional B3LYP [16, 17, 18] as implemented in the CRYSTAL package [19]. The calculations reported here are all-electron, i.e., with no shape approximation to the ionic potential or electron charge density. The geometry optimizations are performed using the algorithm proposed by Schlegel *et al* [20]. The crystalline wave functions are expanded in Gaussian basis sets of double valence quality (6-21G* for C and 864-11G* for Sc). Atomic charges are estimated using Mulliken population analysis [21]. The system is modelled as a one dimensionally periodic array and reciprocal space sampling is performed on a Monkhorst-Pack grid containing 30 symmetry irreducible k-points which converges the total energy to within 10^{-4} eV per unit cell.

Fig.1 (a) shows the calculated electronic eigenspectrum for the relaxed Sc@C_{82} molecule. Sc has three valence electrons and the ground state of Sc@C_{82} is found to be a spin-1/2 system. The unpaired electron occupies the highest occupied molecular orbital (HOMO) of Sc@C_{82} , which constitutes the spin qubit. The HOMO-LUMO gap is 0.530 eV. The separation between the HOMO and (HOMO-1) is 0.789 eV. Therefore, the HOMO is well separated from the energy levels above and below leading to a well-defined qubit. The Sc@C_{82} HOMO is delocalized across the fullerene cage as depicted in Fig.1 (b), which is in agreement with the results found in Ref. [5, 22]. Furthermore, we establish that the HOMO of Sc@C_{82} is virtually identical to the (LUMO+1) of C_{82} , as shown in Fig.1 (c), whereas the lower lying orbitals are hybrids of Sc and C_{82} . Thus Sc acts as a perfect donor to the C_{82} cage for the HOMO state.

Fig. 2 shows the electronic charge rearrangement following the Sc@C_{82} encapsulation in the (14,7) nanotube. The charge depletion from the nanotube is concentrated around the fullerene sites. Similar qualita-

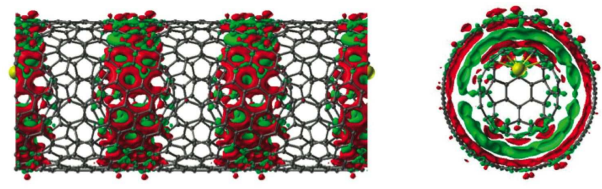


FIG. 2: (Color online) Charge transfer in $\text{Sc@C}_{82}@(14,7)$ peapod. Values for dark grey (red online) and light grey (green online) surfaces are $\pm 0.001 e/\text{\AA}^3$. Left (right) hand shows front (side) views. The atom colored in light grey (gold online) is Sc.

tive results are obtained for the (11,11) nanotube, resembling that in $\text{La@C}_{82}@(17,0)$ [9]. Table 1 shows the charge and spin populations in Sc@C_{82} , $\text{Sc@C}_{82}@(14,7)$ and $\text{Sc@C}_{82}@(11,11)$ peapods. In Sc@C_{82} , 1.64 electrons transfer from the Sc atom to the C_{82} cage indicating a partially covalent Sc-cage bond. In both $\text{Sc@C}_{82}@(14,7)$ and $\text{Sc@C}_{82}@(11,11)$ peapods, electron transfer occurs from the nanotube and the Sc atom to the C_{82} cage due to hybridization between the occupied states of the nanotube and fullerenes. The charge transfer from the Sc atom to the C_{82} cage in $\text{Sc@C}_{82}@(14,7)$ and $\text{Sc@C}_{82}@(11,11)$ is very similar to that of Sc@C_{82} . The electron spin distribution is also similar as 97% of the density resides on the C_{82} cage and only 3% on the Sc atom. The shape of the spin density distribution in the peapods closely resembles that of the HOMO of Sc@C_{82} illustrated in Fig. 1 (b). The charge transfer and spin distribution are insensitive to encapsulation.

Table 1. Charge and spin populations in Sc@C_{82} , $\text{Sc@C}_{82}@(14,7)$ and $\text{Sc@C}_{82}@(11,11)$ peapods

System	Component	$q(e)$	$m(\mu_B)$
Sc@C_{82}	Sc	1.64	0.03
	C_{82}	-1.64	0.97
$\text{Sc@C}_{82}@(14,7)$	Sc	1.63	0.03
	C_{82}	-1.76	0.97
	tube	0.13	0.00
$\text{Sc@C}_{82}@(11,11)$	Sc	1.63	0.03
	C_{82}	-1.70	0.97
	tube	0.07	0.00

In the predicted ground state configuration of the peapods, the spin direction alternates along the Sc@C_{82} chain; the corresponding configuration with parallel spins being higher in energy. We denote these configurations as antiferromagnetic (AF) and ferromagnetic (FM) states, respectively. Both states are found to be Mott insulators and have a total energy lower than the nonmagnetic state. For the $\text{Sc@C}_{82}@(14,7)$ peapod where the inter-fullerene spacing is 3.42 Å, the energy difference between the nonmagnetic and FM states is 0.108 eV/cell. The exchange parameter J , defined as the

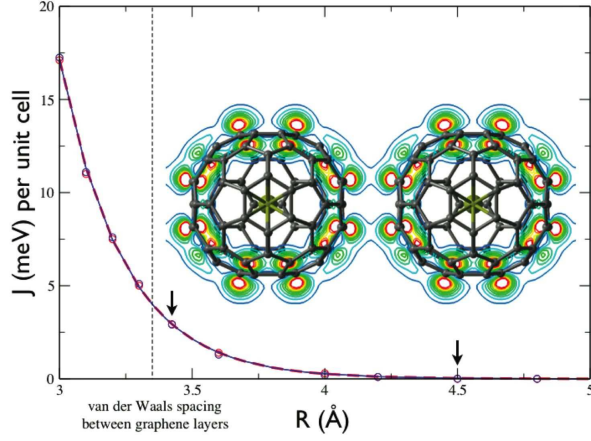


FIG. 3: (Color online) Exchange interaction strength, J , as a function of inter-fullerene separation for a chain of Sc@C_{82} fullerenes. Empty circles refer to calculated results and are fitted using exponential decay law (lines) of the form $J_0 e^{-\lambda(R-R_0)}$, where $J_0 = 4.0$ meV, $\lambda = 4.16 \text{ \AA}^{-1}$, $R_0 = 3.35 \text{ \AA}$. Dashed (red online) line refers to J obtained from the DFT energy difference between FM and AF states. Solid (blue online) line refers to J_{eff} obtained from the Heisenberg model $4t^2/U_{\text{eff}}$, where U_{eff} is fitted to be 0.412 eV from the value of J at R_0 . Arrows show discrete values of R at which J is calculated for peapods. Inset shows electron density contributed by highest occupied states of Sc@C_{82} chain. Range of isovalues is 0-0.002 $e/\text{\AA}^3$.

energy difference between FM and AF configurations, is 3 meV per cell (containing two spins). The behavior of J as a function of the inter-fullerene separation, R , in a Sc@C_{82} chain is plotted in Fig. 3. Values of J calculated for the peapods at discrete values of R , as indicated in Fig. 3, coincide with those obtained for the Sc@C_{82} chain within the accuracy of the present calculations. At these separations the inter-molecular spin interaction is therefore via direct exchange between fullerenes, with a negligible contribution from interactions via the nanotube. This inter-molecular coupling is much larger than the classical dipole coupling of N@C_{60} [23] and even larger than that computed for defective fullerenes with inter-cage links [24], ensuring $> 10^3$ two-qubit gate operations within the decoherence time. This surprising result follows from the HOMOs in the Sc@C_{82} chain being very extended as illustrated in Fig. 3. The p_z orbitals on the closest C atoms belonging to adjacent molecules overlap in a σ -type fashion. This implies that the exchange interaction could be tuned by varying the separation between the fullerenes in peapods, for example by using functionalized fullerenes [25]. Such high J values are consistent with recent magnetic susceptibility experiments on Sc@C_{82} solids [26], which show AF Curie-Weiss temperature $\simeq 300$ K, consistent with $J = 17$ meV at $R = 3.08 \text{ \AA}$ in Fig. 3, which corresponds to the mea-

sured lattice spacing.

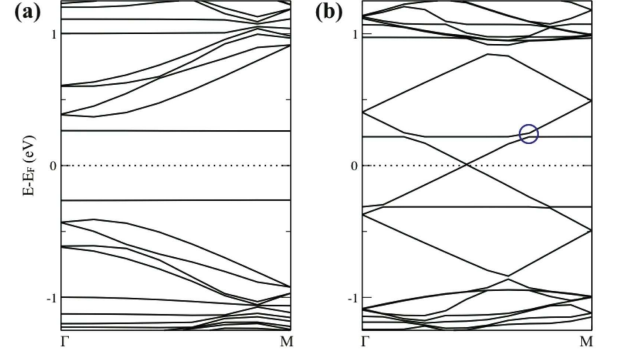


FIG. 4: Spin-polarized band structures of the (a) $\text{Sc@C}_{82}@(14,7)$ and (b) $\text{Sc@C}_{82}@(11,11)$ peapods for the AF configuration. E_F is the Fermi energy.

A generic Hubbard-Anderson model, going beyond DFT and capable of describing the low-energy spin interactions, is conjectured and the energy parameters of this model are estimated by direct comparison of its mean-field solutions with the DFT results. The Hubbard-Anderson model may be used directly to estimate the Heisenberg exchange between spins along the fullerene chain and the Kondo exchange interaction between localized spins on the fullerenes and spins of propagating electrons or holes in the nanotube. The Hamiltonian is

$$H_{HA} = \sum_{lk\sigma} \epsilon_{lk} c_{lk\sigma}^\dagger c_{lk\sigma} + \sum_{k\sigma} E_k a_{k\sigma}^\dagger a_{k\sigma} + \sum_{lk\sigma} \gamma_{lk} [a_{k\sigma}^\dagger c_{lk\sigma} + h.c.] + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (1)$$

where $c_{lk\sigma}^\dagger$ is a creation operator for an electron in the nanotube with band l with quasi-momentum k , $a_{k\sigma}^\dagger$ is a creation operator for an electron in the highest occupied fullerene band, γ_{lk} is the hybridization parameter between fullerenes and nanotube, U is the intra-fullerene Coulomb repulsion energy and n_i is the number operator for the site i of the Sc@C_{82} chain.

The AF band structures of the peapods are plotted in Fig. 4. They display a very narrow but almost perfect cosine form for the highest occupied band [15]. This is well described by a simple tight-binding model with the dispersion energy $\tilde{E}_k = E_0 - 2\tilde{t}\cos k$. It may be shown from an AF mean-field solution of the Hubbard model, that this dispersion corresponds to $E_k = E_0 - 2t\cos k$ in Eq. (1), where $t = \sqrt{\tilde{t}U}$, and $U \simeq 0.53$ eV is obtained from the energy gap between centres of the highest occupied and lowest unoccupied bands in Fig. 4. This solution is also equivalent to a Stoner model for exchange $I = U$, where $J = 4t^2/U$ [27]. The behavior of the computed hopping parameter, t , as a function of R , in a Sc@C_{82} chain is fitted by an exponential decay law of the

form $t_0 e^{-\lambda(R-R_0)}$, where $t_0 = 20.3$ meV, $\lambda = 2.08$ Å⁻¹, $R_0 = 3.35$ Å, showing t^2 and J scaling in the same way. For the values of R in the (14,7) and (11,11) peapods, $t = 17$ meV and 2 meV, respectively.

An effective U is fitted by fixing $J = 4t^2/U_{\text{eff}}$ within the Heisenberg model at R_0 , giving $U_{\text{eff}} = 0.412$ eV, in good agreement with the DFT calculations. Fig. 3 shows that J_{eff} and J are indistinguishable, implying approximately constant U over the range of R considered. U deduced from the DFT band gap is consistent with the mean-field solution of the Hubbard-Anderson model and the total energy difference between FM and AF solutions. With $t \ll U$ for the peapods considered, we thus expect strongly correlated electron effects with well-defined spin-qubits along the Sc@C₈₂ chain of the peapods and weak charge fluctuations. Therefore, the system is well characterized by an antiferromagnetic Heisenberg model.

In the metallic peapod, we may also estimate the hybridization coupling parameters γ_{lk} in Eq. (1) from the anticrossing gaps associated with the nanotube bands and a narrow fullerene band. For example, the anticrossing shown in the inset in Fig. 4 (b) yields a coupling energy $\gamma_{lk} = \Delta E/2 = 5$ meV, where ΔE is the energy gap.

The weak interaction between electrons on the fullerenes and conduction electrons (or holes) in the nanotube, characterized by γ_{lk} discussed above, will give rise to Kondo-like coupling between spins on the fullerenes and spins in the metallic nanotube. The energy scale for these couplings is given by $J_K \sim \gamma_{lk}^2/E_t$, where E_t is a charge transfer energy gap, i.e. $E_t = E_0 + U - E_F$ or $E_F - E_0$ [28]. This gives a typical $J_K \sim 0.1$ meV for the (11,11) peapod.

DFT calculations cannot resolve the difference in J obtained for a Sc@C₈₂ chain and the corresponding peapod structure even at large inter-fullerene separation. This is consistent with direct exchange dominating RKKY interactions. Charge fluctuations could be increased by either enhancing the hybridization interaction through a decrease in the fullerene-nanotube separation, or by tuning the Fermi energy in metallic nanotubes to approach the mixed valence regime in which the charge transfer energy tends to zero. This would enhance both the Kondo coupling and the RKKY interaction, in competition with the direct Heisenberg exchange.

In conclusion, the perfect doping mechanism of Sc@C₈₂ leads to well-defined spin-qubits on the C₈₂ cage in the peapods considered, coupled via antiferromagnetic Heisenberg exchange interaction. For the semiconducting case, the upper and lower Hubbard bands of the fullerene chain are little affected by the nanotube and occur entirely within the band gap of the nanotube, allowing excitations of the Sc@C₈₂ chain independently of the nanotube. Remarkably, in the use of spin peapods for quantum technologies, the main function of the nanotubes will be to give mechanical support for the endohedral fullerenes and to protect them from the environment,

rather than to provide controlled interactions between the spins. An endohedral fullerene peapod thus provides a candidate nanostructure for spin-chain quantum computing [6, 7].

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- [1] D. Loss and D. P. DiVincenzo, Phys. Rev. A **57**, 120 (1998).
- [2] B. W. Smith, M. Monthieux, and D. E. Luzzi, Nature **396**, 323 (1998).
- [3] A. Ardavan *et al*, Phil. Trans. R. Soc. Lond. A **361**, 1473 (2003).
- [4] R. Kitaura and H. Shinohara, Japanese Journal of Applied Physics **46**, 881 (2007).
- [5] G. W. Morley *et al.*, Nanotechnology **16**, 2469 (2005).
- [6] S. C. Benjamin and S. Bose, Physical Review A **70**, 032314 (2004).
- [7] J. Fitzsimons, L. Xiao, S. C. Benjamin, and J. Jones, Physical Review Letters **99**, 030501 (2007).
- [8] S. C. Benjamin *et al.*, J. Phys.: Condens. Matter **18**, S867 (2006).
- [9] Y. Cho, S. Han, G. Kim, H. Lee, and J. Ihm, Phys. Rev. Lett. **90**, 106402 (2003).
- [10] S. Okada, S. Saito, and A. Oshiyama, Phys. Rev. Lett. **86**, 3835 (2001).
- [11] T. Okazaki, T. Shimada, K. Suenaga, Y. Ohno, T. Mizutani, J. Lee, Y. Kuk, and H. Shinohara, Appl. Phys. A **76**, 475 (2003).
- [12] M. Otani, S. Okada, and A. Oshiyama, Phys. Rev. B **68**, 125424 (2003).
- [13] O. Dubay and G. Kresse, Phys. Rev. B **70**, 165424 (2004).
- [14] M. H. Du and H. P. Cheng, Phys. Rev. B **68**, 113402 (2003).
- [15] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, 1998).
- [16] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
- [17] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- [18] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
- [19] V. R. Saunders *et al.*, *CRYSTAL06 Users Manual* (University of Torino, 2006).
- [20] H. B. Schelegel, J. Comput. Chem. **3**, 214 (1982).
- [21] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).
- [22] J. Lu, X. Zhang, X. Zhao, S. Nagase, and K. Kobayashi, Chem. Phys. Lett. **332**, 219 (2000).
- [23] W. Harneit, Phys. Rev. A **65**(3), 32322 (2002).
- [24] J. Chan *et al.*, Phys. Rev. B **70**, 041403 (2004).
- [25] T. W. Chamberlain, A. Camenisch, N. R. Champness, G. A. D. Briggs, S. C. Benjamin, A. Ardavan, and A. N. Khlobystov, J. Am. Chem. Soc. **129**, 27 (2007).

- [26] Y. Ito *et al.*, Chem. Phys. Chem. **8**, 1019 (2007).
- [27] D. G. Pettifor, *Bonding and Structure of Molecules and Solids* (Oxford University Press, 1995).
- [28] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, 1993).